

Structure of C-stabilized fcc Fe on diamond: Epitaxial growth of austenite

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Fe films were grown on single-crystal diamond substrates and the structure and chemistry of the Fe near neighbor environment was studied. It was observed that the Fe is in a metastable fcc structure after a 350° anneal, and a compression of the lattice in the plane of the surface of $1 \pm 0.6\%$ was obtained by comparing low-energy electron diffraction and extended x-ray absorption fine-structure results. Auger-electron spectroscopy shows that C begins diffusing into the fcc Fe lattice at approximately 200 °C. It was observed that the C signal saturates at the equivalent of 1 atom/unit cell in the Fe film, and that the C atoms reside in the octahedral site, as expected for an austenite structure.

The growth-structure-property relationship of metastable face-centered-cubic Fe (γ -Fe) has been the subject of much interest in the last several years. The wide interest shown for Fe stems from the variety of structural and magnetic phases that exists in Fe as thin films, small precipitates, as well as in the bulk form. At room temperature, pure bulk Fe exists as a ferromagnetic, body-centered-cubic (bcc) structure, it adopts an antiferromagnetic fcc structure above 911 °C, while at still higher temperatures, >1392 °C, it reverts back to a bcc structure that is paramagnetic.¹ In recent years many researchers have stabilized γ -Fe by growing it epitaxially on an appropriate template, such as Cu or diamond,²⁻⁵ and found a wide variety of interesting structural and magnetic properties,⁶⁻⁹ one of the most surprising being the indication that thin fcc-Fe films grown on diamond may be ferromagnetic.¹⁰ Growth of these films on diamond is also relevant, due to the increased interest in growing metal contacts onto the surface for use in electronics applications.¹¹ While it is difficult to grow typical contact metals such as copper on the diamond surface, it has been shown that a thin layer of fcc-Fe makes a stable buffer layer for the subsequent epitaxial growth of copper contacts.¹⁰ Copper and diamond surfaces are a good match of γ -Fe because the lattice parameters, 3.61 Å and 3.57 Å, respectively, closely match that of γ -Fe, 3.59 Å. It is well known that up to eight atomic percent of C diffuses into γ -Fe to form austenite,¹² and at an optimal concentration of about 3% C, this phase is stable down to about 700 K. While previous work has concentrated on the stabilization of pure Fe films, in this work, we explore the possibility of incorporating the C into the Fe film by allowing it to diffuse up from the substrate during the annealing cycle, thus growing a metastable Fe-C binary system, i.e., austenite.

In recent work,^{5,10} it has been shown that at low temperature growth and annealing conditions films of γ -Fe could be stabilized via epitaxy on a C(100) substrate up to 18 Å, or about 10 ML. The as-deposited films, which are greater than 10 ML undergo a transition into the more stable bcc phase.^{13,14} In this study, we show that when thinner samples are annealed at temperatures

>200 °C, significant carbon diffusion into the Fe film occurs, and this carbon can stabilize the fcc structure of Fe to higher thicknesses. In order to achieve this structure, we grow the Fe films incrementally on the diamond at low temperature, and at each increment the film is annealed to high enough temperature to allow it to crystallize and let C from the substrate diffuse in and stabilize the fcc phase before more Fe is deposited onto the sample. These studies provide insight into the structure of carbon stabilized γ -Fe films grown on diamond, as well as the structure of the Fe/diamond interface. In addition, we find that these γ -Fe films are stabilized by the carbon to thicknesses substantially greater than 10 ML.

The samples studied here consist of 4 to 24 Å of Fe on C(100). The C(100) substrate was initially cleaned with an acid etch, and then hydrogen terminated by boiling in hydrogen peroxide. Before growth, the substrate was heated to 800 °C, and a 2×1 reconstruction was observed. Fe was then sublimed from an effusion cell onto the C(100), which was held at room temperature. Structural analysis was performed as the samples were annealed, which consisted of angle resolved Auger-electron spectroscopy (ARAES) and I/V low-energy electron diffraction (LEED) analysis. Before breaking vacuum, a 100 Å Cu cap layer was evaporated in order to protect the films from oxidation, and the films were removed from the chamber for the extended x-ray absorption fine-structure (EXAFS) studies. It was observed that the Cu grew epitaxially on the Fe as judged by LEED analysis, in agreement with Ref. 5. The Fe thickness was measured *in situ* using a quartz crystal oscillator and confirmed *ex situ* using Rutherford backscattering spectroscopy.

Immediately after the films were grown at room temperature, Auger-electron spectroscopy (AES) showed that there was no detectable trace of oxygen contamination before or after the annealing, and it was observed that the carbon peak decreased exponentially with Fe thickness. The samples were then annealed, and the Fe/C AES peak ratio was monitored. The AES data from an 11 Å film are shown in Fig. 1, where a sharp drop is observed in the Fe/C ratio between 150 and 200 °C. This indicates that C atoms are diffusing up from the Fe/C

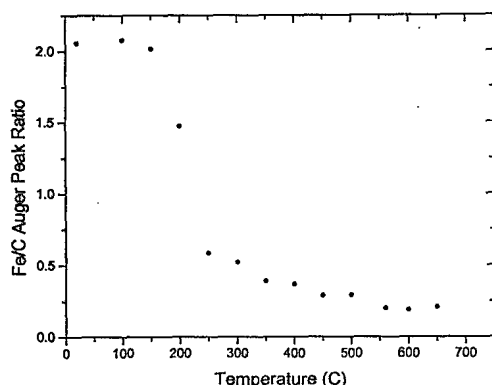


FIG. 1. The Fe/C Auger peak intensity versus annealing temperature shows that carbon begins diffusing into the Fe film between 150 and 200 °C.

interface through the Fe film. The LEED patterns and ARAES data taken from the film after the anneal showed that the Fe is in a single-crystal, fcc structure. According to the phase diagram, the C diffusing into the Fe lattice should aid in the stabilization of the γ -Fe. To test this, a film was grown using 6 Å layers of Fe that were deposited and annealed to 350 °C in four intervals. We achieved a total of approximately 24 Å of single-crystal γ -Fe in this manner, as evaluated by ARAES. The results of the ARAES study from the 24 Å film are similar to those of Ref. 5, and are not shown here. This final thickness is greater than the value of 18 Å, where pure fcc Fe reverts back to its more stable bcc state. The key to growing these films thicker than 18 Å was the incremental growth of thin layers, which allowed the C to diffuse into the γ -Fe, before the pure Fe was thick enough to collapse into its stable bcc phase. This indicates that continuous growth of Fe on C(100) at high temperature may also allow the C to diffuse into the Fe, resulting in thick γ -Fe films, which are essentially single-crystal austenite.

In order to fully characterize these films, we have probed the local environment of the Fe atoms *in situ* with LEED and *ex situ* with EXAFS. The lattice constant perpendicular to the Fe film was obtained by measuring the I/V LEED intensity of the (00) beam at an angle of incidence of $5 \pm 0.01^\circ$ from a 4 ML film, which had been annealed to 350 °C, thus crystallizing the film and allowing the C to interdiffuse into the films. Using Bragg's third condition, we determined the peak order of diffraction (n), plotted energy versus n^2 , and obtained the lattice constant by measuring the slope of this plot. This data is shown in Fig. 2 for a 6 Å Fe film, with the raw I/V data and E vs n^2 plotted in panels (a) and (b), respectively. As seen in Fig. 2(b), an out-of-plane lattice constant of 3.59 ± 0.01 Å is obtained, which is the same as the room-temperature extrapolated value of 3.59 Å for γ -Fe.

In order to investigate the average local atomic structure and chemistry around the Fe atoms in the plane of the films, we have conducted extended x-ray absorption fine structure (EXAFS) from a 4 ML Fe film that was grown in the same manner as the sample studied by IV/LEED. The EXAFS data encompassing the Fe K absorption edge were collected on the Naval Research Laboratory's beamline, X23B, at the National Synchrotron

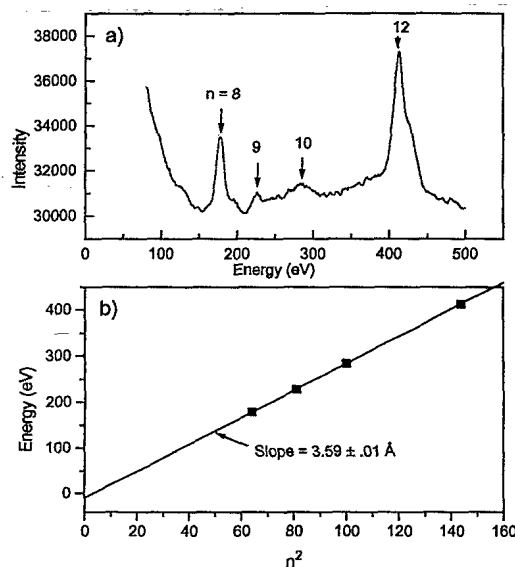


FIG. 2. (a) LEED IV curve of the specular spot from Fe/diamond. (b) The plot of energy vs n^2 . A lattice constant of 3.59 ± 0.01 Å is determined from the slope of the curve.

Light Source (Brookhaven National Laboratory, Upton, NY). Data were collected at room temperature using a conversion electron technique, where the sample is used as the cathode in a He gas ionization cell. In this technique, the total yield of electrons emitted by the sample surface from the competing core-hole decay processes are detected. Details of this data collection scheme and the performance of the detector used here have been presented in Ref. 15.

During data collection, the incident synchrotron radiation was aligned normal to the sample plane, collimated, and focused to a 0.5×0.5 mm² spot size. Because the EXAFS signal has a \cos^2 dependence with respect to the electric field vector of the linearly polarized synchrotron radiation, this geometry probes mainly the in-plane structure around the absorbing atoms. Collection of data in a glancing angle geometry, which would have provided information weighted towards the out-of-plane structure, was not possible due to the small sample area (≈ 6 mm²) and volume and to the reduced signal when the beam is further collimated.

Following established EXAFS analysis procedures,¹⁶ the fine-structure extending from about 20–600 eV above the absorption edge was normalized to the edge step height and energy, and a low-frequency background curvature was removed. These data were then converted to photoelectron wave vector space, and are presented in Fig. 3. For comparison purposes, spectra collected from fcc-Cu and bcc-Fe standards, which were similarly analyzed, are also shown. A qualitative comparison between these data illustrates that a better match of both the relative amplitude and the phase exists between the Fe/C(100) and the fcc-Cu standard. Small variations in the relative amplitude and phase can be attributed to differences in the local chemistry around the absorbing atoms between the Cu standard and the Fe/C sample. Alternatively, the Fe/C and the bcc Fe data have much less in common.

To better illustrate the real space structure around Fe

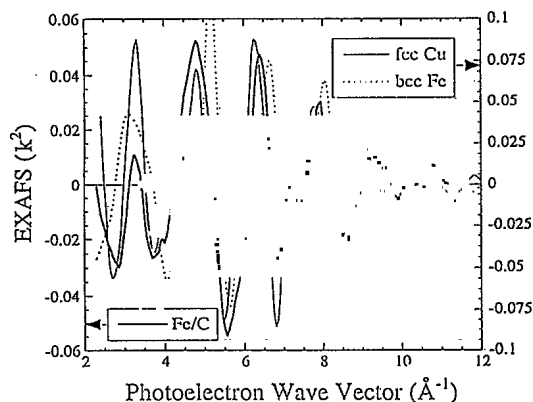


FIG. 3. Representation of the Fe/C(100) EXAFS data in photoelectron wave vector (k) space after normalization and removal of background curvature. Similar data from a fcc Cu and bcc Fe standards are presented for comparison.

atom sites, the Fe EXAFS data were Fourier transformed to radial coordinates. Figure 4 is a plot of the Fourier transformed Fe EXAFS data collected from the 6 Å Fe/C sample, together with similarly analyzed data collected from Fe in a bcc-Fe standard, and the fcc Cu. These data were Fourier transformed using a k range of 2.0 to 11 Å and a χ^2 weighting. Since the data has not yet been corrected for electron phase shifts, the Fourier peak positions do not correspond with the true bond lengths, but are instead shifted to lower radial distances by an amount equal to the electron phase shifts, which are unique to the pair correlations. All of these data have been normalized to the near neighbor amplitude and vertically offset, to allow for a visual comparison of the relative amplitude and distance of the higher order peaks appearing over a range of 3 – 5 Å. Illustrations of the bcc and fcc unit cells, presented in the inset, correlate the unit cell positions with the Fourier features. The four atomic sites nearest the absorbing atom within the fcc unit cell are represented in the Fe/C(100) data, showing that the Fe is indeed in a face-centered structure, similar to the fcc-Cu standard.

To extract more quantitative information about the average local environment around the Fe atoms, the region of the Fourier transform from 1.5–2.75 Å was isolated and back-Fourier transformed to photoelectron wave vector space. This operation serves to isolate those EXAFS data which contribute to the near neighbor environment of the absorbing atom. These data were then fit using parametrized theoretical EXAFS spectra, generated using the FEFF (3.11) codes of Rehr and co-workers.¹⁷ The FEFF EXAFS spectra were refined by fitting to empirical standards of Fe₂C, fcc Cu, and bcc Fe in order to improve the measurement of the E_0 -correction (–3 eV) and the EXAFS amplitude reduction coefficient (0.64). Initially, the data were fit using a single shell of Fe atoms, however, a significantly improved fit was achieved using an additional shell of Cu atoms to simulate the Cu/Fe interface. The best fit to these data, as judged by a least squares fitting parameter, is illustrated in Fig. 5 (presented in photoelectron wave vector space). The fitted data represent two correlations superimposed on one another; one being the Fe-Fe correlation at a distance of 2.51 ± 0.02 Å, and the other being the Fe-Cu correlation at a distance of

2.62 ± 0.02 Å. From the average Fe-Fe distance, we obtain an in-plane lattice constant of 3.55 ± 0.02 Å, which corresponds to $\approx 1\%$ reduction compared to the perpendicular spacing, which was measured by LEED I/V curves.

The peak appearing near 1.4 Å in the Fe/C EXAFS data arises from the C neighbors in the film. An Fe-C distance of 1.84 ± 0.02 Å was determined by fitting the r -space range from 1.0 to 1.74 Å. To provide an additional check, this data range was fit using both FEFF-generated EXAFS data and experimental EXAFS data collected from the Fe₂C standard. The latter was useful, because the Fe-C correlation in that sample also appears as a resolved peak in its Fourier transform. We find that our measured Fe-C bond length is significantly shorter than those tabulated for the intermetallic compounds Fe₂C (1.98 Å) and Fe₃C (2.14 Å). However, our measured value is in agreement with the value of 1.84 ± 0.02 Å reported in Ref. 18, for the minimum Fe-C distance in FeC solid

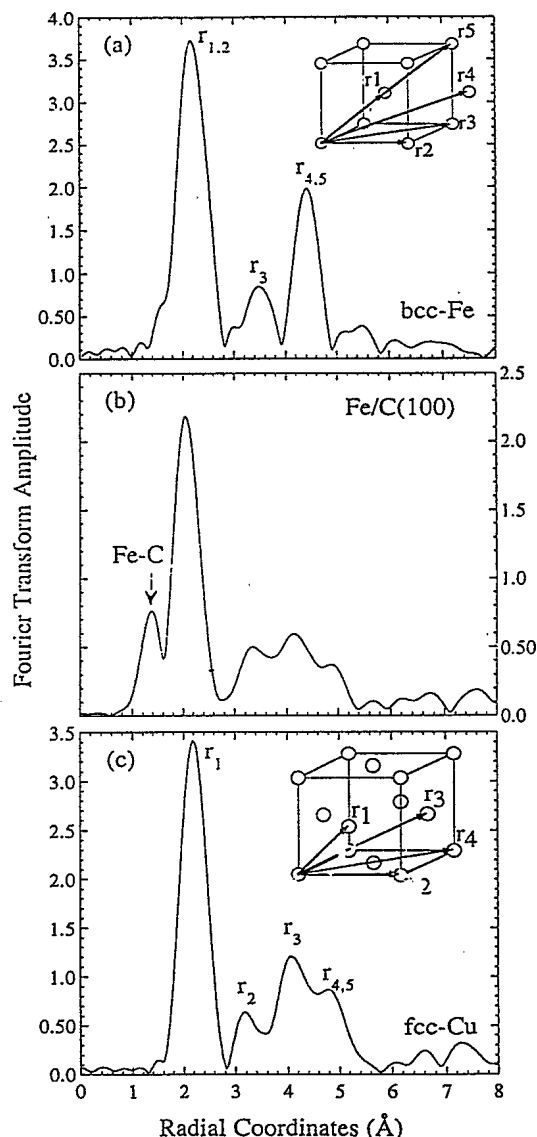


FIG. 4. The Fourier transformed (i.e., a real space representation) Fe EXAFS data compared to fcc-Cu and bcc-Fe standards. All data have been normalized with respect to the near neighbor peak and vertically offset for clarity. The Fourier transforms were performed using a k^2 -weighting and identical k -space ranges for all of the data sets.

solutions. Hence, an interpretation of the data in terms of the formation of the Fe-C intermetallic compounds near the interface is inconsistent with the EXAFS results and analysis presented here. Rather, this bond length corresponds to the austenite structure, with the C atoms residing in the octahedral sites of the γ -Fe lattice.

Finally, the measured average coordination around Fe atoms is 2.7 ± 1 C atoms. In the case of perfect interfaces, we expected to find 7 C neighbors around each interfacial Fe atom,¹⁹ giving an average of 1.75 C atoms around each Fe atom (for this four atomic layer film). The measured coordination of 2.7 C atoms, therefore, corresponds to 1 C atom/fcc unit cell (8%) included in the γ -Fe film. This, in connection with the fcc-Fe structure and the fact that the C resides in the octahedral site, shows that these films have the austenite structure.

In conclusion, we have performed LEED, AES, and EXAFS studies on thin Fe films epitaxially grown on diamond (100) substrates. We find that for a thickness of up to at least 24 Å the Fe is stabilized in an fcc structure by C diffusion from the Fe/C interface. The EXAFS data shows that the 4 ML films are in the austenite structure, and the in-plane lattice constant is 3.55 ± 0.02 Å, while the out of plane lattice constant, measured *in situ* with LEED, is 3.59 ± 0.01 Å. This gives a tetragonal distortion of $1 \pm 0.6\%$, which is slightly less than the 3% tetragonal distortion measured for the fcc-Fe films on diamond in Ref. 5. These films are very stable and can be used as a seed for subsequent growth of, e.g., very thick films of epitaxial copper.¹⁰ The determination of the atomic structure and the carbon diffusion is critical to the determination of the electronic structure modeling of this system. We hope that this study will provide impetus to further work on the magnetic, electronic, and structural

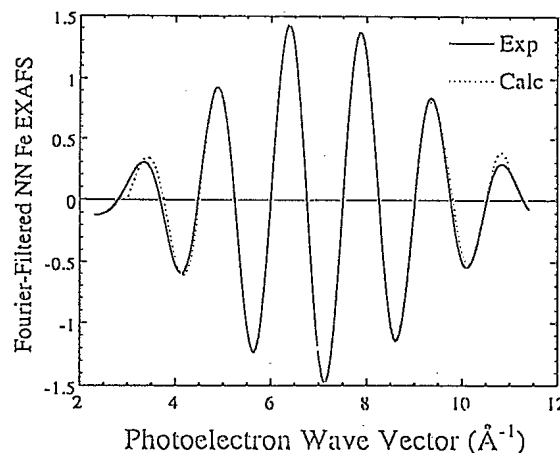


FIG. 5. Back-Fourier transformed near neighbor Fe EXAFS and the best fit obtained using FEFF-generated standards. An r -space range of 1–3 Å was used in the back-Fourier transform. Parameters used to obtain best fit are described in the text.

properties of this system.

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- ¹⁹ The coordination at the C interface is calculated here assuming that the Fe sits in a hollow site. The seven neighbors then arise from three shells, four in the topmost C layer, two in the interpenetrating fcc lattice of the diamond structure, and one directly below, at the face center of the topmost diamond fcc lattice. These three shells have nearly equal bond lengths, and would be indistinguishable in the present experiment.